

# A study of performance of corrosion prevention compounds on AA2024-T3 with electrochemical impedance spectroscopy

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## Abstract

The performance of corrosion prevention compounds (CPC) on AA2024-T3 was assessed with electrochemical impedance spectroscopy (EIS). The good correlation between the protection performance of CPC and both the interfacial impedance and double layer capacitance allowed two assessment criteria to be defined; as found for AA7075-T6, excellent protection was exhibited by CPC-coated surfaces with interfacial impedances above  $0.1 \text{ M}\Omega \text{ cm}^2$  or double layer capacitances below  $7.6 \times 10^{-8} \text{ F/cm}^2$ . A correlation between double layer capacitance ( $C_{dl}$ ) and corroded area was also obtained. This latter correlation offers an alternative to evaluation of CPC performance via the corroded area calculated from  $C_{dl}$ . In addition, a prediction method was demonstrated based on impedance parameters that showed the feasibility of using data from 30 days to predict the performance of CPC after 180 days exposure. It was found that the CPC failure can be greatly accelerated without changing the relative ranking among the CPC used by introducing intentional scratches on CPC-coated specimens. In particular, the minimum time needed to rank various CPC was reduced to 8 days for scratched specimens from several months for unscratched ones.

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**Keywords:** Corrosion prevention compounds; Interfacial impedance; Double layer capacitance; Corroded area determination

## 1. Introduction

Corrosion prevention compounds (CPC) are materials that can both prevent new corrosion sites from forming as well as suppress corrosion that has initiated. They are widely used on aircraft as a relatively inexpensive way of protecting against corrosion at compromised areas of the coating systems and in occluded regions [1]. CPC are often classified according to their ability to displace water and the appearance of the film after application (e.g., water-displacing; hard film, waxy). Although CPC have been widely used for decades, no generally accepted test methodology exists for assessing or screening CPC performance for aerospace applications. Specifications have generally focused on easily measured physical and chemical properties, including compatibility with other materials and safety.

Various salt spray tests have long been used for assessing organic coatings, but there is persistent dissatisfaction with the correlation between such tests and the performance in more benign field applications [2,3]. More recently, sensitive electrochemical methods have been shown to allow coating system performance to be assessed in environments that mimic service or in actual service itself. Thus, instead of attempting to greatly accelerate the damage and thereby risk altering the damage mode responsible, a more sensitive measurement of the degradation allows less aggressive, but more relevant, solutions to be used.

Because of its non-invasive nature and its ability to discriminate coating performance, electrochemical impedance spectroscopy (EIS) has been widely used as a non-destructive technique to study organic coatings on metals to gain complementary information to that obtained by traditional methods for characterizing the behavior of organic coatings in corrosion environments [4–8]. In studies of epoxy-coated steel and an epoxy-coated magnesium alloy, Scully and Hens-

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ley found a correlation between the magnitude of the low frequency impedance and long-term coating deterioration [9,10]. In other work, Hack and Scully [11] used EIS to quantify the defect area of organic-coated steels in seawater via the breakpoint frequency method. Other applications of EIS to the study of organic coating include the monitoring of water uptake under cyclic wet–dry condition with coating capacitance [12] and its use on the study of corrosion behavior of internally coated metal containers [13]. In addition, EIS also has been used to assess long-term exposure behavior of coatings on steel immersed in seawater. The relative performance ranking after 2 years exposure was paralleled by determined by EIS, although it seems that EIS alone is not adequate for evaluating blistering of organic coatings where the blisters develop between the coating layers [14].

The present study demonstrates the level of protection provided by CPC for aluminum alloys and the ability of parameters derived from EIS measurements to both assess and predict CPC performance on these aerospace materials. In the present context, assessment quantifies protection, whereas prediction describes the ability to use short-term measurements to forecast long-term performance. A method described predicts the long-term performance of CPC using parameters extracted from short-term test data. Comparisons are made between the impedance behavior of CPC and that of typical organic coatings, demonstrating that not all impedance analyses that provide insight for organic coatings are applicable to CPC.

## 2. Experimental

### 2.1. Specimen preparation

The specimens used in this work were cut to 7.62 cm × 7.62 cm (3 in. × 3 in.) from an aluminum alloy (AA) 2024-T3 sheet with a thickness of 0.229 cm (0.090 in.) and composition of (wt%): Cu 3.8–4.9, Mg 1.2–1.8, Mn 0.3–0.9, Ti ≤ 0.15, Zn ≤ 0.3, Fe ≤ 0.5, Si ≤ 0.5, Ni ≤ 0.1, and (Fe + Ni) ≤ 0.5. Each specimen was cleaned by sequentially degreasing in an ultrasonic bath with acetone for 5 min and methanol for another 5 min, rinsing in high-purity water, and finally drying in air. A flat electrochemical cell was used for impedance measurements. The area of the specimen in contact with the O-ring used to seal the cell was taped with 63.5 μm thick polyester tape to avoid damage to the CPC film. The total exposed area was 13.1 cm<sup>2</sup>. Four commercial CPCs were studied in this work: Amlguard (LHB Industries, St. Louis, MO), Dinitrol® AV30, Dinitrol® AV8 (DINO-LAB, Hässleholm, Sweden), and LPS3 (LPS Laboratories Inc., Tucker, GA). These CPC cover the range of US military specifications (MIL-C-85054) as well as Boeing materials specifications (BMS3-23 and BMS3-29). The film types of CPC chosen here include three that form hard, dry films (Amlguard, AV8 and AV30) and one that forms a waxy film (LPS3). All were applied by spraying. After application of

the CPC, all specimens were allowed to dry overnight before exposure to the solution. The thickness for dry CPC films was between 15 and 20 μm. In some cases, local penetration of the dried CPC was made with a knife to create X-shaped scratches on the surface in order to test damaged surfaces.

### 2.2. Exposure methods

The lap joint simulation solution (LJSS) was used as the exposure solution with composition as follows [15]: 20 mM NaCl, 4 mM NaHCO<sub>3</sub>, 4 mM NaNO<sub>2</sub>, 2 mM NaF, adjusted to pH 9. This solution has been shown to mimic that found in isolated occluded regions that are widespread on aircraft. Constant and alternate immersion exposures were both investigated. Alternate immersion involved cycles of immersion in the LJSS for 12 h followed by drying in the air for 12 h.

### 2.3. Electrochemical impedance spectroscopy

EIS spectra were generated as a function of exposure time. Each spectrum was obtained after monitoring of the open circuit potential (OCP) for 1 h. Spectra were generated after 2 and 5 days and then once a week thereafter. Later, the test time interval increased with increasing exposure time. The spectra for scratched AA2024-T3 under constant immersion was generated every day then stopped after 2 weeks of immersion. The EIS measurements were performed using a Solatron SI 1260 impedance/gain-phase analyzer in combination with a Solatron 1287 electrochemical interface. The frequency range used was 100 kHz to 10 mHz, and the voltage amplitude was 7 mV rms. For samples exposed to alternate immersion, EIS was performed at the end of the wet portion of the cycle.

Interfacial impedance was used to characterize the resistance of CPC film to corrosion. It was obtained by subtracting the resistance of the solution from the impedance magnitude measured at the lowest tested frequency (10 mHz). Polarization resistance ( $R_p$ ) and double layer capacitance ( $C_{dl}$ ) values were obtained by fitting the impedance spectra to equivalent circuit models with ZView® (Scribner Associates, Southern Pines, NC). The equivalent circuit models used were generally of the form shown by Beaunier et al. [16] and Mansfeld et al. [17], although in some cases, a Warburg element was added to improve the fit. The electrochemical parameters, such as polarization resistance and double layer capacitance, were extracted from the fitted data. The fitting quality was controlled by the fitting error. Generally, the fitting was considered as good when the fitting error for each parameter was less than 10%, and such good fits were generally easily achieved. Note that the polarization resistance is always the same or less than the interfacial impedance as defined, with the difference being due to impedance related to mass transport processes. The percentage of corroded area was calculated from digital images of the scratched specimens using the image processing software package AnalySIS® (Soft Imaging System, Lakewood, CO).

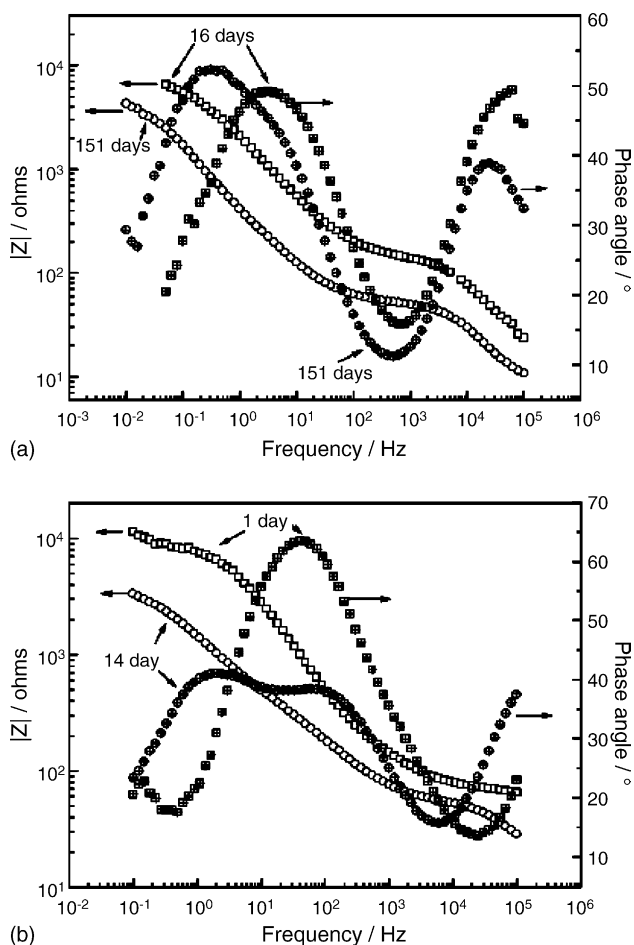


Fig. 1. The evolution of spectra for (a) Amlguard-coated AA2024-T3 under constant immersion in LJSS and (b) scratched Amlguard-coated AA2024-T3 under constant immersion in LJSS.

### 3. Results

Fig. 1 shows the evolution of the spectra for the CPC-coated non-scratched (a) and scratched (b) Amlguard-coated AA2024-T3 under constant immersion after various exposure times. There is a substantial decrease in the overall impedance over the exposure time. The shift in the spectra with time is much larger than that was observed with the unscratched samples, even though the exposure time for scratched specimen is much shorter. Corresponding sample images are shown in Fig. 2.

Fig. 3 shows the changes in the interfacial impedance with exposure time for AA2024-T3 under alternate immersion. The figure illustrates that interfacial impedances decreased with exposure time. Comparing the data in Fig. 3 to that from constant immersion, it was found that the CPC performances are independent of exposure method, with larger decreases resulting from alternate immersion. All CPC-treated specimens initially had substantially higher interfacial impedances than the control (uncoated) sample. The interfacial impedance of the control was unaffected by the nature

of the exposure, remaining at approximately between 5 and  $10 \text{ k}\Omega \text{ cm}^2$  throughout, as shown in Fig. 3.

It is worth noting that although the broad qualitative trends were the same for different alloys and exposure methods, the relative performance of the CPC depended somewhat upon exposure method. For example, for times longer than about 50 days of alternate immersion, the AV8-treated specimen had lower interfacial impedance than the Amlguard-treated specimen (Fig. 3), whereas under constant immersion the interfacial impedance values of AV8 and other two CPC were found to be higher than that of Amlguard.

It was found that  $C_{dl}$  and  $R_p$  also reflect the decay of CPC performance with exposure time, as shown in Fig. 4 for Amlguard and LPS3, which represent the worst and the best CPC studied in this work, respectively. Obviously, the trend of  $R_p$  is quite similar to that of interfacial impedance, while  $C_{dl}$  shows the opposite trend with time, increasing due to the initiated corrosion after exposing for certain time. The relationship between  $C_{dl}$  and time was further studied in the study of CPC performance on scratched AA2024-T3 and will be discussed in more detail later.

CPC failure can be facilitated by the creation of intentional defects. In this work, such defects were introduced by scratching the CPC-treated specimen. Fig. 5 shows the increase in the corroded area on the scratched samples with the exposure time for AA2024-T3 under constant exposure as determined by image analyses. The CPC-treated specimens had visible corrosion after only 3 days' exposure, with the exception of LPS3. Compared to the unscratched samples, these observations demonstrate rapid acceleration of detectable degradation. Although the corroded area increased with the exposure time in all cases, the rate of increase for the different CPC varied. The LPS3-treated specimen had the best performance at all times and Amlguard-treated specimen had the worst performance at most times.

Unlike what was found for scratched, CPC-coated AA7075-T6, in which there was little change of the interfacial impedance with time under constant immersion [18], for scratched AA2024-T3, there were slight changes of the interfacial impedance with time, especially for AV8 and Amlguard-coated specimens, as seen in Fig. 6. Thus, the interfacial impedance does indicate the decay of CPC performance on this alloy. However, the double layer capacitance showed very dramatic changes with exposure time (and increases in corroded area). As shown in Fig. 7, large increases in  $C_{dl}$  were observed for all CPC-treated scratched specimens that exhibited corrosion. Fig. 8 shows the linear relationships found between  $C_{dl}$  and corroded area for scratched, CPC-coated AA2024-T3 under constant immersion. In general, the linear relations were good, with  $R^2$  between 0.76 and 0.97 for different CPC.

Data shown in Figs. 3–8 are for CPC-treated AA2024-T3. Qualitatively similar behavior was observed for AA7075-T6 samples coated with the same CPC [18]. A similar ordinal ranking of CPC performance to that found for AA2024-T3 was found. As with AA7075-T6, AV8 exposed to alternate

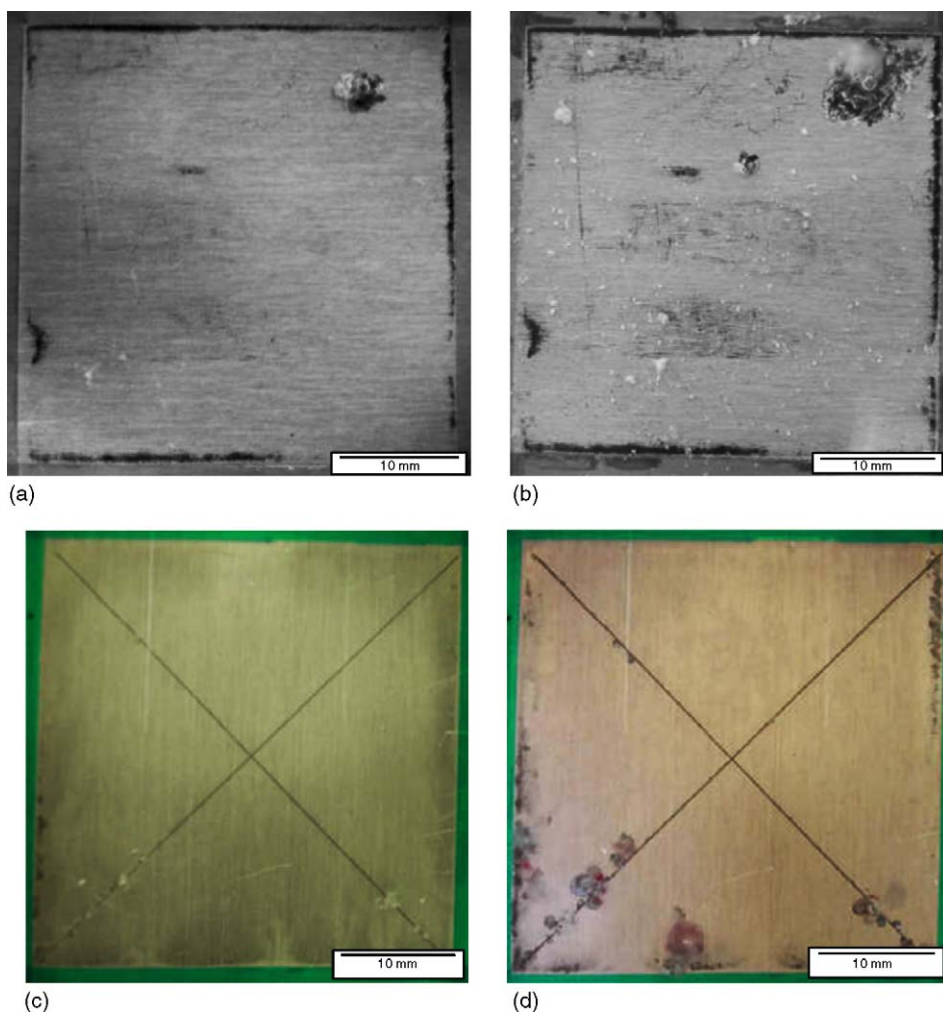


Fig. 2. The sample images with exposure time corresponding to the EIS spectra in Figs. 1 and 2. (a) Amlguard-coated AA2024-T3 under constant immersion for 19 days, (b) Amlguard-coated AA2024-T3 under constant immersion for 163 days, (c) Amlguard-coated scratched AA2024-T3 after 1-day exposure to constant immersion, and (d) Amlguard-coated scratched AA2024-T3 after 2 weeks constant immersion.

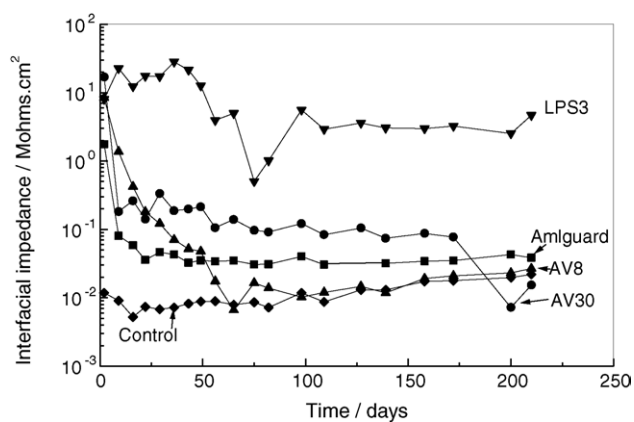


Fig. 3. The evolution of the interfacial impedance for CPC-coated AA2024-T3 under alternate immersion in LJSS.

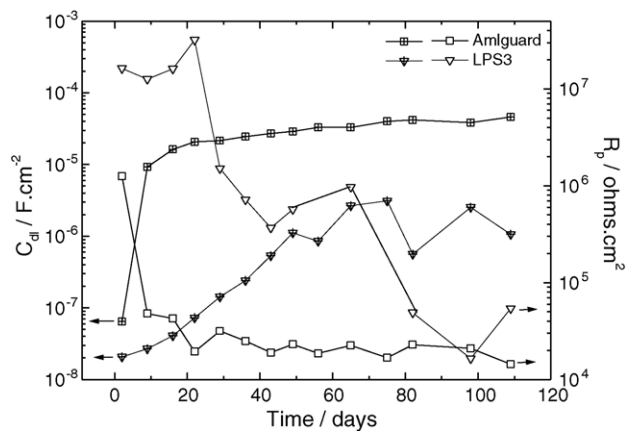


Fig. 4. The double layer capacitance ( $C_{dl}$ ) and the polarization ( $R_p$ ) vs. time for CPC-coated AA2024-T3 under alternate immersion in LJSS.



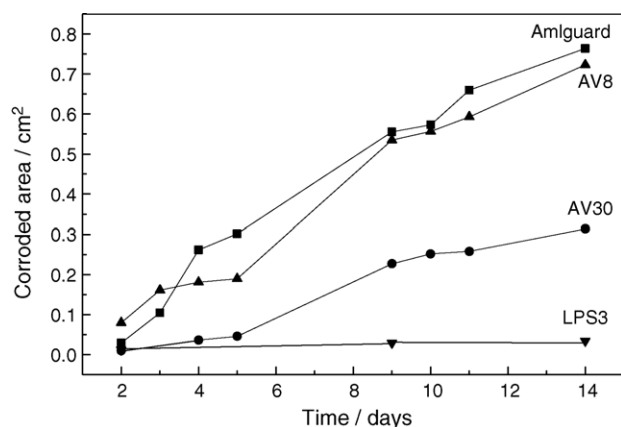


Fig. 5. The increase of corroded area with exposure time for scratched, CPC-coated AA2024-T3 under constant immersion in LJSS.

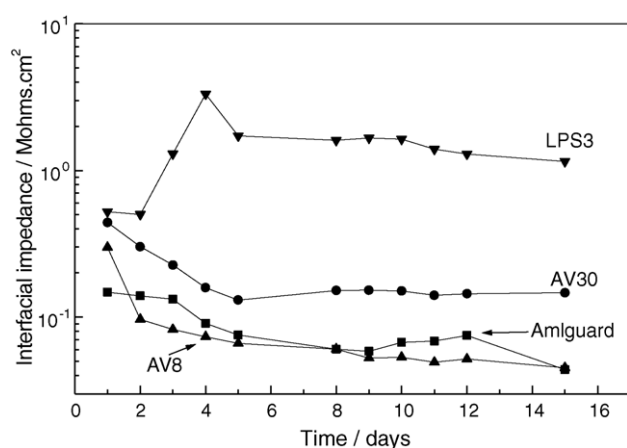


Fig. 6. The evolution of the interfacial impedance of scratched, CPC-coated AA2024-T3 specimens under constant immersion in LJSS.

immersion was also found to perform the worst among the CPC tested for reasons discussed later.

The primary protection provided by the CPC studied was through the formation of a barrier film rather than through release of strong inhibitors or buffering of the local solu-

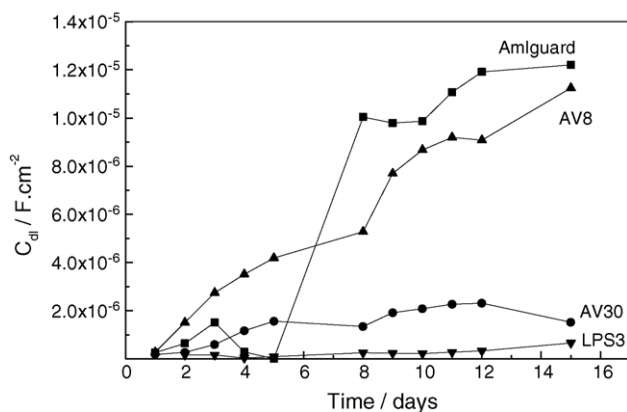


Fig. 7. The double layer capacitance ( $C_{dl}$ ) vs. time for scratched, CPC-coated AA2024-T3 under alternate immersion in LJSS.

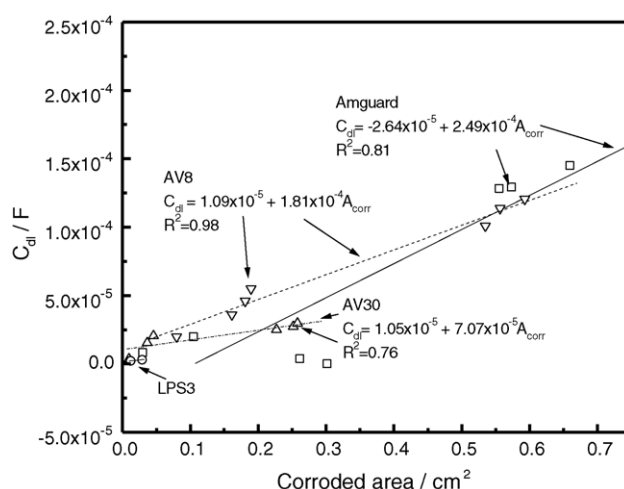


Fig. 8. The correlation between double layer capacitance ( $C_{dl}$ ) and corroded area ( $A_{corr}$ ) on scratched, CPC-coated AA2024-T3 specimens under constant immersion in LJSS.

Table 1  
Buffering strength

Solution	1N HCl acid ( $\mu$ L)
LJSS in sealed bottle	150
Amlguard	120
AV30	120
AV8	120
LPS3	110
LJSS exposed to air for 13 days	110

tion pH. Experiments showed that neither the changes in pH values nor the interfacial impedance of AA2027-T3 in leachates were significant for any of the CPC studied. The pH changes were at most one unit in the acidic direction, well within the stability region of the Al passive film, so this change is not overly deleterious. The interfacial impedances of AA2024-T3 in all CPC leachates were below 200 k $\Omega$  cm<sup>2</sup> and did not increase with leaching time. Some interfacial impedances of AA2024-T3 exposed to the leachates were slightly higher (a factor of 2–5) than the control, but showed no systematic increase with time, as would be expected for a leaching inhibiting species. In addition, the buffer abilities of the CPC leachates were obtained by measuring the pH change of leachate when titrated with 1N HCl. The volume of HCl needed to change the pH from 9 to 3 represents the buffer strength of the solution, as shown in Table 1.

## 4. Discussion

### 4.1. Protection of aluminum alloys by CPC as a barrier film

The objective of field application of CPC is to provide short-term protection for aluminum alloy structures to obviate the need for the time-consuming task of repainting. Therefore, it is important to determine the extent to which CPC pro-

vide protection to aerospace alloys. Fig. 3 demonstrates that the interfacial impedance for CPC-coated specimens is initially substantially higher than that of the control specimens for both alloys exposed to either exposure protocol (constant immersion or alternate immersion). Although the degree of protection varies with the specific CPC/alloy/exposure combination, the initial impedance is in all cases more than an order of magnitude above the control. For example, several CPC-coated samples have initial interfacial impedances greater than  $10 \text{ M}\Omega \text{ cm}^2$ , which is on the order of protective epoxy coatings [19].

The predominant difference between true organic-based paints and most CPC is in the perseverance of the protection. Good organic coating systems are known to provide protection for years in full-immersion in seawater [9,10,14,20], whereas most of the CPC studied here lost a substantial portion of their protection ability within 30–50 days of either alternate or constant immersion in LJSS, although in several cases, some protection is maintained out to 180 days. The tradeoffs for the lower performance are the lower cost and the ease of application of the CPC relative to repainting the structure. CPC are not meant to be replacements for organic coating systems, but are meant to temporarily protect exposed metal at large coating defects that develop in service. The lower level of performance of CPC is not only to be expected, but also should be considered in the selection of the CPC.

In this study, the ordinal ranking of the performance of CPC on AA2024-T3 was generally  $\text{LPS3} > \text{AV30} > \text{AV8} > \text{Amlguard}$ . However, this ordinal ranking was not followed strictly in all situations. For example, as mentioned above, AV8-coated AA2024-T3 specimen performed no better than Amlguard after 50 days exposure under alternate immersion. However, for constant immersion on AA2024-T3, AV8 showed fairly good performance. Comparing the photographs taken during testing, it was found that a substantial portion of the CPC film on the AV8-treated AA2024-T3 under alternate immersion had been washed off after about 2 months exposure when replenishing solution during the wet and dry cycles. The gradual loss of the CPC film under alternate immersion led to its poor performance.

#### 4.2. Ability of CPC to modify electrolyte corrosivity

Most CPC formulations are proprietary, but their low cost has precluded the inclusion of expensive inhibitors. Instead, low-cost inhibitors, such as phosphates and sulfonates, have been included at reasonably low levels in an effort to provide some level of active protection.

As mentioned above, no systematic change in the impedance of AA2024-T3 in the leachates with leaching time was observed, although there are some differences existing between various CPC. As a matter of fact, the best CPC that was found on bold exposure, LPS3, cannot distinguish itself from the others in terms of the effects of the leachate solu-

tions. In addition, the buffering ability test on the leachate indicated that the differences between CPC are very small. As shown in Table 1, it is clear that the buffer strength of the leachates, defined as the volume of the acid needed to adjust the solution pH from 9 to 3, was nominally the same for all of the leachates. Therefore, inhibitor leaching has little effect on the buffer ability of the solution. It can be concluded at this point that the inhibitor leaching does not have significant modification on the electrolyte and hence the function of CPC. The CPC provide protection via the formation and maintenance of a blocking film that prevents large-scale interactions of cathodes and anodes on the specimen surface.

#### 4.3. CPC performance assessment metric

The CPC tested here were observed to fail by either localized corrosion initiation, blister formation, or peeling of a portion of the film. While any of these could be detected via visual observation, assessment by this means is work-intensive and can be subjective. Quantitative image analysis can be performed, but for efficient, rapid screening, a quantitative parameter derivable from analyses of EIS data that correlated with CPC performance was sought.

As stated above, for any CPC and alloy combination, the interfacial impedance generally decreased while the CPC performance decayed based on visual inspection. Thus, the interfacial impedance had a qualitative correlation with CPC performance during the exposure time period independent of the exposure method, alloy, and CPC.

Comparison of the interfacial impedance versus time data with visual observations allowed a quantitative interfacial impedance criterion to be defined as a CPC performance indicator. The CPC could be regarded to have failed if the value of interfacial impedance fell below the criterion. It is important to understand that the failure is defined here as the presence of a visual indication of corrosion. In practice, CPC reapplication time depends on both the extent of the damage and the effect that damage would have on the structural integrity of the component. In this work, the interfacial impedance of  $0.1 \text{ M}\Omega \text{ cm}^2$  was chosen for the performance criterion. The selection of this value was based on the observation that CPC-treated specimens showed visible corrosion sites after the interfacial impedance fell below  $0.1 \text{ M}\Omega \text{ cm}^2$ . Generally, there were several corrosion sites once the interfacial impedance of a specimen reached just below  $0.1 \text{ M}\Omega \text{ cm}^2$ . After that, the interfacial impedance of certain CPC-coated specimen would stabilize, such as Amlguard, while some would decrease with the time due to an increasing number of corrosion sites developed or due to the loss of a portion of CPC film, such as was the case for AV8. Among the CPC studied, AV8 behaved somewhat differently than the others in that interfacial impedance went below  $0.1 \text{ M}\Omega \text{ cm}^2$  after an exposure of 50 days under alternate immersion while it stayed above  $0.1 \text{ M}\Omega \text{ cm}^2$  during the entire test period under constant immersion. As stated above, it was found that the specimen started to lose a portion of the CPC film under alter-

nate immersion and corrosion spots initiated after 50 days exposure. After that time, the corrosion started to propagate so that the interfacial impedance went below  $0.1 \text{ M}\Omega \text{ cm}^2$ .

It is worth noting that the interfacial impedance for AV30-treated specimen was just above  $0.1 \text{ M}\Omega \text{ cm}^2$  after exposure for 50 days under alternate immersion as shown in Fig. 3. However, in this case, AV30-coated specimen had no visible corrosion sites initiated on the surface. Instead, a large number of small blisters had developed on the specimen uniformly, but the CPC film still provided protection. Eventually, when the remainder of the film was lost, corrosion initiated on the surface, and the impedance fell below  $0.1 \text{ M}\Omega \text{ cm}^2$ . Similar behavior was observed for CPC-treated AA7075-T6 under alternate immersion [18].

When corrosion occurred at the interface of CPC and the aluminum substrate, not only did the impedance decrease, but also the double layer capacitance increased. The double layer capacitance reflects the area over which a fully developed metal/solution or delaminated interface exists [21,22]. Fig. 8 shows the correlation between  $C_{dl}$  and corroded area that represents a physical measure of CPC performance. Linear fittings for Amlguard, AV30, and AV8 were obtained with  $R^2$  between 0.76 and 0.97.

These equations are useful in terms of the assessment of the CPC performance either in the laboratory or in the field. Given a measurement of the  $C_{dl}$ , one can calculate the corroded area without the need for tedious image acquisition and analysis. The corroded area so determined can be used to judge whether a typical CPC has failed sufficiently to be reapplied based upon the extent of corrosion acceptable for the given situation. For example, in some applications, the only impact of several square centimetres of corroded area is a loss of cosmetic appearance, and that may not be of sufficient importance to reapply the CPC or repair the structure. For highly stressed components, even a small amount of corrosion may be unacceptable as the corrosion could serve as a site for crack initiation. Based on the data in Fig. 8, a  $C_{dl}$  value of  $1 \times 10^{-6} \text{ F}$  ( $7.6 \times 10^{-8} \text{ F/cm}^2$ ) could be used as a failure criterion, as all CPC-treated samples that exceeded that value went on to exhibit extensive growth of corrosion.

It is important to know that the corroded/delaminated area has not been found to be correlated to a single impedance parameter in all cases. Instead, there are cases where the breakpoint frequency has correlated with damaged area [11], and others where the coating capacitance has been found to be a reflection of water uptake [9,23]. In the absence of such a universally applicable parameter, such correlations must be developed on a case-by-case basis.

#### 4.4. Rapid screening testing for CPC

During exposure of nominally pristine CPC-treated samples, the relative performance ranking was not clear until after exposing for a relatively long time, especially for constant immersion exposure. In fact, the full performance ranking process took close to 6 months of exposure under constant

immersion. Obviously, this approach does not allow rapid screening of CPC, although it may be useful in estimating reapplication intervals. In addition, in many applications, the CPC may experience physical damage after application. The robustness of the CPC to such damage is of interest, and it presents an alternative means of testing.

The acceleration of CPC failure by the application of cross scratches is clearly demonstrated in Fig. 5. Corrosion occurred on all CPCs except the LPS3-treated specimen after only a few days, as opposed to the weeks needed for visually detectable damage to occur in the unscratched samples. Fig. 2 also illustrates this observation, showing that the damage accumulated in 163 days during constant immersion on the pristine sample (a and b) can be reproduced around the scratches (c and d) after constant immersion of only 2 weeks. It was also found that the time for similar degree of corrosion in the case of scratched specimens was much shorter than that of non-scratched specimens in alternate immersion, even though it was found in this work that alternate immersion is more aggressive than constant immersion. The acceleration and simplification (constant immersion rather than alternate immersion) make the scratched electrode approach attractive.

The scratched specimen testing allowed CPC performance to be more easily ranked with a much shorter exposure time. For example, the data shown in Fig. 5 allowed the CPC performance to be ranked after only a few days as  $\text{LPS3} > \text{AV30} > \text{AV8} > \text{Amlguard}$ , while this ranking of performance order was not obvious until exposure for at least 50 days for alternate immersion and even longer for constant immersion. Note that the performance rank of order in the case of scratched specimens is the same as that obtained for the nominally pristine samples. This suggests that the scratching merely accelerated the CPC failure rather than altering the failure mode.

#### 4.5. Prediction of CPC performance

One of the pressing needs in the use of CPC is the prediction of their performance as a function of the alloy/CPC combination. As shown above, usually it takes a substantial time to observe the entire performance decay process. Therefore, in addition to an assessment tool, a prediction method would be of great use.

In this work, several potential predictors were assessed by attempting to correlate the parameter values at short times to the interfacial impedance values of the same specimens at long times (180 days). The predictors considered were the interfacial impedance, the double layer capacitance, the coating capacitance, and the coating resistance. Data from CPC-treated AA7075-T6 [18] are included in the following analyses.

Fig. 9 shows the relation found for nominally pristine samples between interfacial impedance at 50 days and interfacial impedance after 180 days. Generally, higher impedance after 50 days predicts better CPC performance after 180



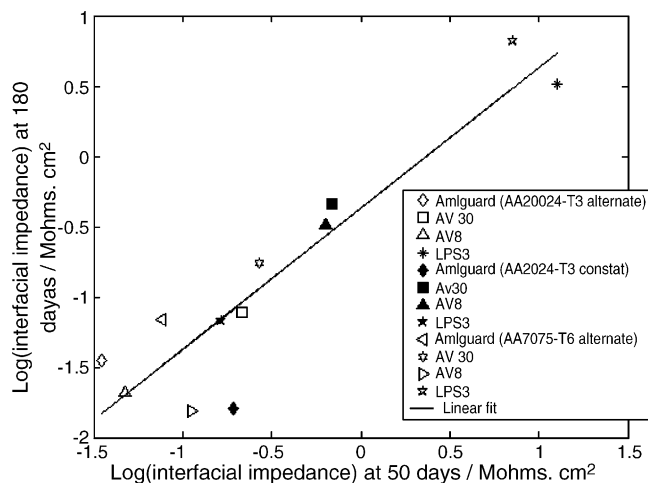


Fig. 9. The correlation between interfacial impedance at 50 days and that at 180 days for AA2024-T3 and AA7075-T6 coated with different CPC and exposed to either AI or CI.

days. In Fig. 9, LPS3 on AA7075-T6 and on AA2024-T3 under alternate immersion had the highest impedance among all CPC/alloy combinations. In neither case was any corrosion visible after 180 days exposure to the LJSS. However, all other CPC-treated samples with lower impedances at 50 days either showed corrosion to some degree or had a visibly porous film. A reasonable linear relationship was found between short-term low frequency impedance and long-term low frequency impedance. While this correlation would imply that the interfacial impedance could predict CPC performance, it should be noted that when times shorter than 50 days were chosen, there was a poor correlation to 180-day performance. For example, when using the data from 20 days, a relatively poor correlation was obtained with the performance at 180 days, as quantified by an  $R^2$  of only 0.6. As noted above, Scully and Hensley [9,10] found a similar correlation between interfacial impedance and long-term performance of organically coated steel.

Another CPC performance predictor considered was the double layer capacitance obtained by fitting of the EIS data. Fig. 8 demonstrates that a very good correlation was found between  $C_{dl}$  and the corroded area for scratched specimens. On non-scratched samples, a similar relation was found between low-frequency capacitance measured at short times and long-term performance. Fig. 10 shows the correlation between  $C_{dl}$  at 30 days and the interfacial impedance at 180 days as well as the linear fitting result. It indicates that CPC with lower  $C_{dl}$  at 30 days will perform better after 180 days. Thus, the double layer capacitance represents an improvement in prediction ability over the interfacial impedance since 30-day results can predict long-term performance.

The outlier point marked by a circle in Fig. 10, which represents AV8-coated AA7075-T6 exposed to alternate immersion, was not considered in the correlation analysis. As discussed above, the low impedance of that specimen was due to the film of AV8 being washed off when replenishing the solu-

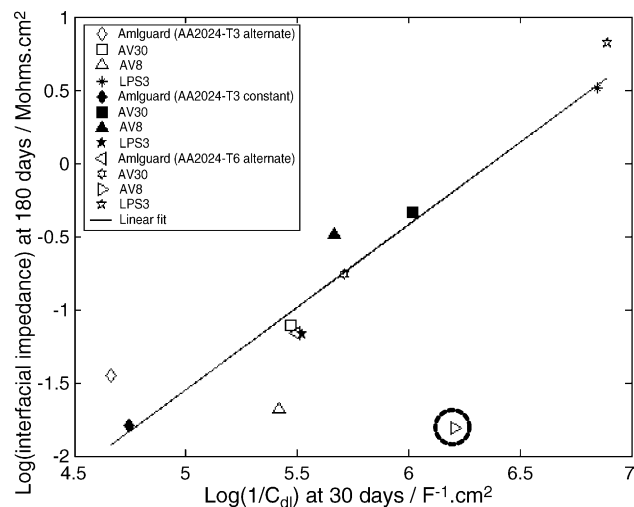


Fig. 10. The correlation between interfacial impedance at 180 days and the inverse of double layer capacitance at 30 days for AA2024-T3 and AA7075-T6 coated with different CPC and exposed to either AI or CI.

tion during wet and dry cycles. Therefore, although showing a higher impedance at 30 days, it did not perform well after 180 days. Other parameters, such as coating resistance and coating capacitance, were also considered but none showed any predictive ability.

## 5. Conclusions

- (1) CPC provide a reasonable degree of protection for AA2024-T3 exposed to lap joint simulation solutions for a limited time, independent of the exposure method.
- (2) The protection provided by the CPC studied here was based on the creation of a barrier rather than any contribution from inhibitor release or modification of the local pH or buffering capacity.
- (3) The interfacial impedance and double layer capacitance on nominally pristine specimen were found to correlate with CPC performance, allowing the definition of two criteria to be used in CPC performance assessment: an interfacial impedance of  $0.1 \text{ M}\Omega \text{ cm}^2$  and a double layer capacitance of  $7.6 \times 10^{-8} \text{ F/cm}^2$ . In addition, the interfacial impedance and the double layer capacitance could be used for the prediction of CPC long-term performance, albeit with modest acceleration factors.
- (4) Intentional scratches can accelerate CPC failure without changing the ranking of CPC, providing a means for rapid CPC screening and assessment.
- (5) The comparison between paints and CPC showed that although there are several parameters available for assessment of paints, only the interfacial impedance and double layer capacitance are useful in assessment of CPC performance. Other parameters, such as coating capacitance and resistance, did not correlate with performance for any of the CPC studied.

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## References

- [1] B. Hinton, Fourth International Aerospace Corrosion and Control Symposium, Jakarta, Indonesia, 1996.
- [2] B.S. Skerry, C.H. Simpson, *Corrosion* 49 (8) (1993) 663.
- [3] O.O. Knudsen, U. Unni Steinsmo, M. Marit Bjordal, et al., *J. Protective Coat. Linings* (December) (2001) 52.
- [4] J.A. Gonzalez, E. Otero, A. Bautista, et al., *Prog. Org. Coat.* 33 (1) (1998) 61.
- [5] J. Kittel, N. Celati, M. Keddad, et al., *Prog. Org. Coat.* 41 (1–3) (2001) 93.
- [6] F. Mansfeld, *Electrochim. Acta* 35 (10) (1990) 1533.
- [7] F. Mansfeld, M.W. Kendig, S. Tsai, *Corrosion* 38 (11) (1982) 570.
- [8] W.S. Tait, *J. Coat. Technol.* 75 (942) (2003) 45.
- [9] J.R. Scully, *J. Electrochem. Soc.* 136 (4) (1989) 979.
- [10] J.R. Scully, S.T. Hensley, *Corrosion* 50 (9) (1994) 705.
- [11] H.P. Hack, J.R. Scully, *J. Electrochem. Soc.* 138 (1) (1991) 33.
- [12] J.H. Park, G.D. Lee, *Corros. Sci.* 45 (8) (2003) 1881.
- [13] W.S. Tait, *J. Coat. Technol.* 61 (768) (1989) 57.
- [14] J.N. Murray, H.P. Hack, *Corrosion* 47 (6) (1991) 480.
- [15] K.S. Ferrer, R.G. Kelly, *Corrosion* 58 (5) (2002) 452.
- [16] L. Beaunier, I. Epelboin, J.C. Lestrade, et al., *Surf. Technol.* 4 (3) (1976) 237.
- [17] F. Mansfeld, M.W. Kendig, S. Tsai, *Corrosion* 38 (9) (1982) 478.
- [18] F. Gui, R.G. Kelly, *Corrosion* 61 (2) (2005) 119.
- [19] H. Leidheiser, *J. Coat. Technol.* 63 (802) (1991) 21.
- [20] C.T. Chen, B.S. Skerry, *Corrosion* 47 (8) (1991) 598.
- [21] J.N. Murray, P.J. Moran, E. Gileadi, *Corrosion* 44 (8) (1988) 533.
- [22] H. Xiao, F. Mansfeld, *J. Electrochem. Soc.* 141 (9) (1994) 2332.
- [23] S. Lin, H. Shih, F. Mansfeld, *Corros. Sci.* 33 (9) (1992) 1331.